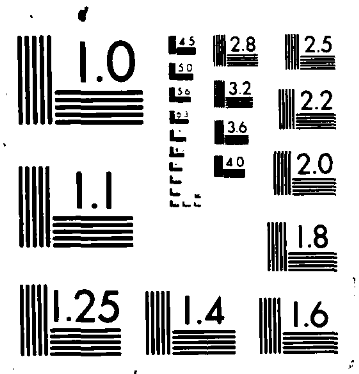
AD-A181 063    IN SITU GRAZING INCIDENCE X-RAY DIFFRACTION STUDY OF    1/1
ELECTROCHEMICALLY DE  (U) PUERTO RICO UNIV RIO PIEDRAS
DEPT OF PHYSICS  M G SAMANT ET AL  12 MAY 87 TR-25
UNCLASSIFIED  N00014-81-C-0776    F/G 7/4    NL

END
7 87
DTIC


1.0
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

DTIC FILE COPY

(12)

AD-A181 063

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|---|---|
| 1. REPORT NUMBER: Technical Report #25 | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle): In Situ Grazing Incidence X-ray Diffraction Study of Electrochemically Deposited Pb Monolayers on Ag(111) | | 5. TYPE OF REPORT & PERIOD COVERED: Interim Technical Report |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s): Mahesh G. Samant, Michael F. Toney, Gary L. Borges, Lesser Blum and Owen R. Melroy | | 8. CONTRACT OR GRANT NUMBER(s): N 00014-81-0776 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS: Physics Department, University of Puerto Rico, Rio Piedras, PR 00931 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Task No. NR-051-0776 |
| 11. CONTROLLING OFFICE NAME AND ADDRESS: Code 572-Office of Naval Research, Arlington, VA 22217 | | 12. REPORT DATE: 5-12-87 |
| | | 13. NUMBER OF PAGES: 16 |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) | | 15. SECURITY CLASS. (of this report): Unclassified |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release
Distribution unlimited

DTIC
ELECTE
JUN 0 9 1987
S D
D

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for publication in Physical Reviews Letters

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

X-ray, electrode, interface, structure

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)


We report here the first in-situ X-ray diffraction measurements from a monoalayer adsorbed at a metal-liquid interface. Diffraction peaks were observed from a monoalayer of lead electrochemicially deposited onto a silver (111) surface immersed in aqueous electrolyte. Grazing incidence geometry was used. The lead was found to order into a closed packed hexagonal structure, compressed 1.2% from bulk lead. The first order diffraction peak was 0.037 $A^{-1}$ broad in the radial and azimuthal directions,


DD FORM 1473, 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

87

cont'd indicating that even in an aqueous environment the Pb monoalayer forms a well ordered two dimensional solid. A rotational epitaxy angle (angle between the Pb and Ag surface lattices) of 4.4° was observed.

| Accesion For | | |
|---|---|---|
| NTIS CRA&I | ☑ | |
| DTIC TAB | ☐ | |
| Unannounced | ☐ | |
| Justification | | |
| By | | |
| Distribution / | | |
| Availability Codes | | |
| Dist | Avail and / or Special | |
| A-1 | | |

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-81-C-0776

TASK No. NR 051-775

TECHNICAL REPORT #25

In Situ Grazing Incidence X-ray Diffraction Study of Electrochemically Deposited Pb Monolayers on Ag(111)

by

Mahesh G. Samant*, Michael F. Toney*, Gary L. Borges*, Lesser Blum** and Owen R. Melroy*

*IBM Almaden Research Center, K34/802
650 Harry Road, San José, CA 95120

**Department of Physics, POB AT, Faculty of Natural Sciences,
University of Puerto Rico, Río Piedras, Puerto Rico 00931

Prepared for Publiacation in Physical Reviews Letters

Reproduction in whole or in part is permitted for any purpose of the United States Government

*This document has been approved for public release and sale, its distribution is unlimited

*This statement should also appear in Item 10 of Document Control Data -- DD Form 1473. Copies of form available from cognizant contract administrator.

# In Situ Grazing Incidence X-ray Diffraction Study of Electrochemically Deposited Pb Monolayers on Ag(111)

Mahesh G. Samant, Michael F. Toney, Gary L. Borges, Lesser Blum[**]

and Owen R. Melroy[*]

IBM Almaden Research Center, K34/802

650 Harry Road, San Jose, CA 95120

Abstract

We report here the first *in-situ* x-ray diffraction measurements from a monolayer adsorbed at a metal-liquid interface. Diffraction peaks were observed from a monolayer of lead electrochemicially deposited onto a silver (111) surface immersed in aqueous electrolyte. Grazing incidence geometry was used. The lead was found to order into a closed packed hexagonal structure, compressed 1.2% from bulk lead. The first order diffraction peak was 0.037 $Å^{-1}$ broad in the radial and azimuthal directions, indicating that even in an aqueous environment the Pb monolayer forms a well ordered two dimensional solid. A rotational epitaxy angle (angle between the Pb and Ag surface lattices) of 4.4° was observed.

---

[*] to whom inquiries should be addressed.

[**] Physics Department, College of Natural Sciences, PO Box AT, Rio Piedras, Puerto Rico 00931

Over the past twenty years there has been an explosion in the number of surface science techniques. These advances have largely been confined to the vacuum/solid interface as most surface structural methods are based on scattering of electrons or ions and hence limited to ultrahigh vacuum (UHV). Our knowledge of the structure of the metal/solution interface is far less detailed. In electrochemistry, for instance, it is well known that the electrode material, the exposed crystal face, and adsorption have pronounced effects on the chemical and physical properties of the interface, but the details are not well understood. There is a vast amount of literature proposing different models for the structure of the interface encompassing both the "compact layer" (the layer of solvent molecules and other species which are believed to be specifically adsorbed to the electrode), and the "diffuse layer" (the layer which contains the excess cations or anions necessary to balance the charge of the electrode and the ions in the compact layer).[1-5] Unfortunately, the experimental data available to date has primarily been based on capacitance measurements[6] which can be only indirectly related to the interfacial structure. More recently, spectroscopic methods such as surface enhanced Raman,[7,8] second harmonic generation,[9,10] infrared spectroscopy[11-13] and others[14] have provided valuable information on the nature and orientation of adsorbed molecules but these yield only indirect information on the geometrical structure of the interface.

UHV based surface science techniques have been brought to bear on the question of the metal/electrolyte interface[15-16] but these are all *ex-situ* measurements and require the transfer of the electrode from the electrochemical environment to vacuum. This operation introduces considerable questions about whether the surface rearranges upon the removal of solvent and loss of potential control during transfer. At the very least, all information on the organization of the solvent at the electrode is lost.

Only an *in-situ* measurement can remove these uncertainties. Because of their long penetration depth in condensed phases and the high flux available from synchrotron sources, X-ray techniques offer a unique opportunity to probe the structure of this interface *in-situ* and on an atomic scale. We have previously used surface extended X-ray absorption fine-structure spectroscopy (SEXAFS) to probe the structure of metal monolayers adsorbed on single crystal electrodes.[17,18] In this letter we report the first observation of grazing incidence X-ray scattering from a solid/liquid interface. Specifically, we have observed diffraction from a monolayer of lead deposited on a silver (111) surface immersed in an aqueous solution.

The deposition of lead on silver (111) occurs in two distinct stages. The first monolayer of lead is deposited over a very narrow potential range at a potential well positive of the Nernst potential for the deposition of $Pb^{2+}$ on a Pb electrode and hence is termed underpotential deposition (UPD).[19] No additional lead is deposited until the potential is poised approximately 150 mV more negative, after which bulk deposition occurs. By clamping the electrode at a potential between the formation of the monolayer and that of bulk lead formation, a stable monolayer is obtained. Assuming that the lead ions are completely discharged, the charge passed during this deposition is consistent with the formation of a two dimensional close packed hexagonal array of lead.[20] Although both reflectance[20] and ellipsometry[21] measurements support this interpretation, no direct structural determination has previously been made.

The silver electrode was prepared by epitaxial vapor deposition of silver onto a cleaved mica substrate[22] and was confirmed to be (111) surface using Laue diffraction. The lead monolayer was deposited from an aqueous 0.5 M sodium acetate, 0.1 M acetic acid, and $5 \times 10^{-5}$ M lead acetate solution (Aldrich Gold label). A schematic of the experimental apparatus and the

electrochemical cell is shown in Figure 1. The electrolyte solution was confined between the electrode and a thin polypropylene film (.5 mil). The monolayer of lead was deposited by poising the silver (111) electrode (A) at -0.53 V vs. a Ag/AgCl (3M KCl) reference electrode (B). A Platinum coil (C) was used as the auxiliary electrode. The electrochemical response from the lead deposition was essentially identical to that previously reported.[20] This shows that the surface is clean, since the UPD phenomena is known to be extremely sensitive to impurity adsorption.[19] After deposition, the cell was changed to a thin layer configuration such that the layer of solution covering the electrode allowed collection of data from the lead monolayer without excessive background from the solution layer itself. Lead was electrochemically removed from the surface and redeposited between diffraction scans.

The data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) under dedicated conditions on a focussed 8-pole wiggler beam line (VII-2). A silicon (111) double crystal monochromator was used to select an incident wavelength of 1.534 Å. The electrochemical cell was mounted on a Huber goniometer head and attached to SSRL's four circle diffractometer with the sample plane vertical during diffraction measurements. All data reported were acquired at a grazing angle where the maximum intensity from the monolayer was observed (0.54° for the air/water/silver interface). The scattered beam was collimated to 0.1 mrad by Soller slits and collected by a scintillator detector. The inset in Figure 1 illustrates the diffraction geometry and defines the appropriate angles.

Figure 2a shows the rocking scan of the (10) reflection from the lead monolayer, which is rotated 4.4° from the Ag (110) direction. This diffraction was confirmed to result from the lead monolayer by repeating the scan with the electrode poised at 0 V, Figure 2b. At this potential, lead is oxidized to $Pb^{2+}$, dissolves in the electrolyte, and the monolayer and its

diffraction peaks are not present. The relatively large background present in both scans is primarily due to diffuse scattering from the thin layer of solution covering the electrode. The scan made in the radial direction for this (10) reflection gives a peak which is similar in both intensity and the breadth to the one shown in Figure 2a. Identical diffraction peaks are observed at 60° intervals consistent with the expected six fold symmetry for a hexagonal layer. The (11) and (20) reflections from the overlayer were also observed, again each with six fold symmetry. From this data, it is clear that the lead monolayer forms a hexagonal closed packed layer and from the diffraction angle, the in-plane nearest neighbor distance was calculated to be 3.459 Å, a 1.2% contraction from the distance in bulk lead (3.501Å). From the full width half maximum (FWHM) of the peak, 0.037 $Å^{-1}$, the size of the lead domains is estimated to be >300 Å. This is comparable to that observed for a lead monolayer on copper (110) in UHV.[23]

In addition to the lead diffraction peaks rotated +4.4° from the corresponding silver direction, a similar peak rotated -4.4° is observed for each reflection. This is shown in Figure 3a and 3b for the (10) and (11) Pb reflections, respectively. A straight line background was subtracted from this data. The intensities of the reflections at +4.4° are different than at -4.4°, which indicates there are either more, or larger domains of one rotation. It should also be remembered that a fresh monolayer was deposited before each scan, so the differences between the (10) reflection and the (11) may not be significant. The origin of this is uncertain, but large differences in the diffraction intensities from different domains have been observed for $O_2$ and $D_2$ on graphite using LEED.[24]

Figure 4 illustrates the proposed close packed monolayer of UPD lead on a silver (111) surface. The open circles represent the underlying silver atoms and the shaded circles the atoms in the

lead overlayer which is incommensurate (the Pb lattice is not simply related to the Ag surface lattice). We assume that the Pb atoms prefer to sit in 3-fold hollow sites where the coordination number is maximized. The rotational epitaxy angle (angle describing the alignment of the overlayer with respect to the substrate) of 4.4° measured experimentally is shown. It is less than the value of 6.5° predicted by the McTague and Novaco model[25] but in excellent agreement with that observed by Takayangi et al.[20] who used LEED to study the vacuum deposition of lead on silver (111). In the McTague and Novaco model, the strain energy of the overlayer is dependent on its orientation relative to the substrate and the overlayer assumes the direction with the lowest energy. The reason for the difference between the predicted and measured angles is unclear at this time. The agreement with the results obtained in UHV is very encouraging, offering the hope that many of the studies in UHV can be directly related to those at the metal/solution interface. It also illustrates that, with care, the cleanliness of the surface required for structural studies in UHV cam be maintained at the metal/solution interface.

In conclusion, this work demonstrates that *in-situ* structural determination at the metal/solution interface is possible using X-ray diffraction. The observation of the (10), (11) and (20) lead reflections show that at full coverage, the overlayer is a hexagonally close packed monolayer, incommensurate with the silver (111) substrate and is compressed 1.2% relative to bulk lead. Although the lead overlayer is incommensurate with the silver, the lead crystal axis is oriented relative to the silver lattice with a 4.4° rotational epitaxy angle observed.

Acknowledgements

This work was partially supported by the Office of Naval Research and was carried out at the Stanford Synchrotron Radiation Laboratory (SSRL) which is supported by the Department

of Energy. We wish to thank Joseph G. Gordon II and Sam Fain for many useful discussions and Sean Brennan for his help with the experimental apparatus at SSRL.

*References*


1. G. Gouy, J. Phys., ***9***, 457 (1910).

2. D. Chapman, Phil. Mag. ***25***, 475 (1913).

3. L. Blum and D. Henderson, J. Chem. Phys., ***74*** 1902 (1981).

4. J. Badiali, M. Rosinberg, F. Vericat and L. Blum, J. Electroanal. Chem., ***158***, 253 (1983).

5. W. Schmickler and D. Henderson, J. Chem. Phys., ***80***, 3381 (1984).

6. R. Parsons and F. Zobel, J. Electroanal Chem., ***9***, 333 (1956).

7. R. Chang and T. Furtak, ***Surface Enhanced Raman Scattering***, Plenum Press, New York, 1982.

8. M. Weaver, F. Barz, J. Gordon and M. Philpott, Surface Science, ***125***, 409 (1983).

9. R. Corn, M. Romagnoli, M. Levenson and M. Philpott, J. Chem. Phys., ***81***, 4127 (1984).

10. G. Richmond, Langmuir, ***2***, 132 (1986).

11. S. Pons, J. Electroanal. Chem., ***150***, 495 (1983).

12. A. Bewick, J. Electroanal. Chem., ***150***, 481 (1983).

13. K. Kinimatsu, H. Seki, W. Golden, J. Gordon and M. Philpott, Langmuir, ***2***, 464 (1986).

14. J. Gordon and S. Ernst, Surface Science, ***101***, 499 (1980).

15. A. Hubbard, Acc. Chem. Res., ***13***, 177 (1980).

16. P. Ross, Surface Science, ***102*** 463 (1981).

17. L. Blum, H. Abruna, J. White, J. Gordon, G. Borges, M. Samant and O. Melroy, J. Chem. Phys., ***85***, 6732 (1986).

18. M. Samant, G. Borges, J. Gordon, L. Blum and O. Melroy, J. Am. Chem. Soc., (in press).

19. D. Kolb in ***Advances in Electrochemistry*** H. Gerischer and C. Tobias, Eds., Vol II, Wiley: New York, 1978, p 125.

20. K. Takayanagi, D. Kolb, K. Kambe and G. Lehmpfuhl, Surface Science, ***100***, 407 (1980).

21. R. Muller and J. Farmer, Surface Science, ***135***, 521 (1983).

22. K. Reichelt and H. O. Lutz, J. Cryst. Grow., ***10***, 103 (1971).

23. S. Brennan, P. H. Fuoss, and P. Eisenberger, Phys. Rev. B, *33* (6), 3678 (1986).

24. M. Toney and S. Fain, (Submitted Phys. Rev. B); J. Chui and S. Fain, private communication.

25. J. P. McTague and A. D. Novaco, Phys. Rev. B, *19* (10), 5299 (1979).

**Figure Captions**

Figure 1. Electrochemical Cell: A) Silver (111) electrode, B) Ag/AgCl reference electrode, C) Platinum counter electrode, D) Polypropylene window, E) O-ring holding polypropylene to cell, F) External electrical connection to sliver electrode, G) Solution inlet, and H) Solution outlet.

Insert: Grazing incidence scattering geometry showing the incident angle $\alpha$, the output angle $\delta$, the scattering angle $\theta$, and theazimuthal angle $\phi$.

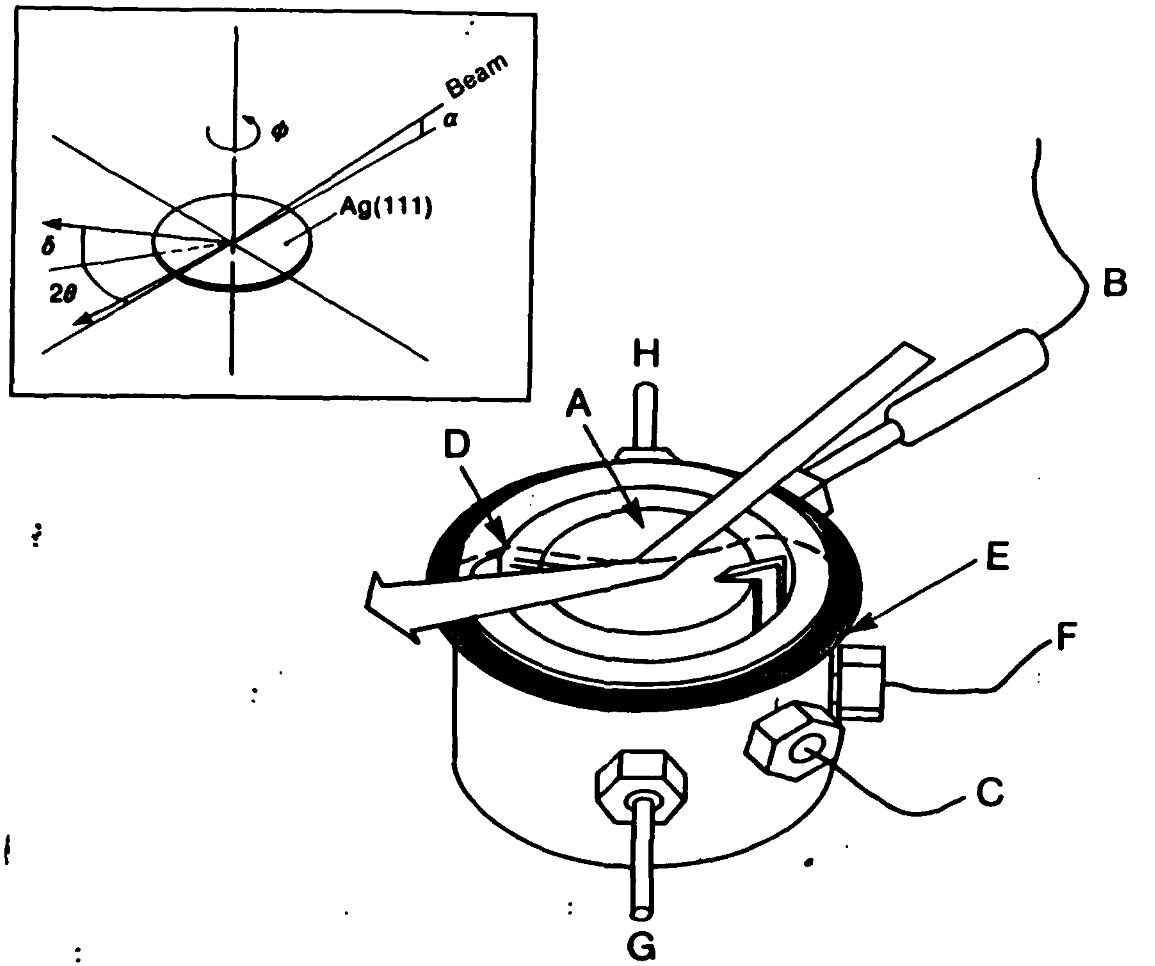
Figure 2. a) Rocking scan ($\theta$ $2\theta$ is fixed) of the lead (10) reflection at a scattering vector of 2.099 $\mathring{A}^{-1}$, corresponding to peak in the radial scans. The silver (110) direction is along $\phi = 330°$

b) Same as 2a but with the electrode held at 0 V.

Figure 3. a) Rocking scans ($\theta$ $2\theta$ is fixed) of the lead (10) reflection at a scattering vector of 2.099 $\mathring{A}^{-1}$, corresponding to the peak in the radial scans. The silver (110) direction is along $\phi = 330°$

b) Rocking scans ($\theta$ $2\theta$ is fixed) of the lead (11) reflections at a scattering vector of 3.603 $\mathring{A}^{-1}$, corresponding to the peak in the radial scans.

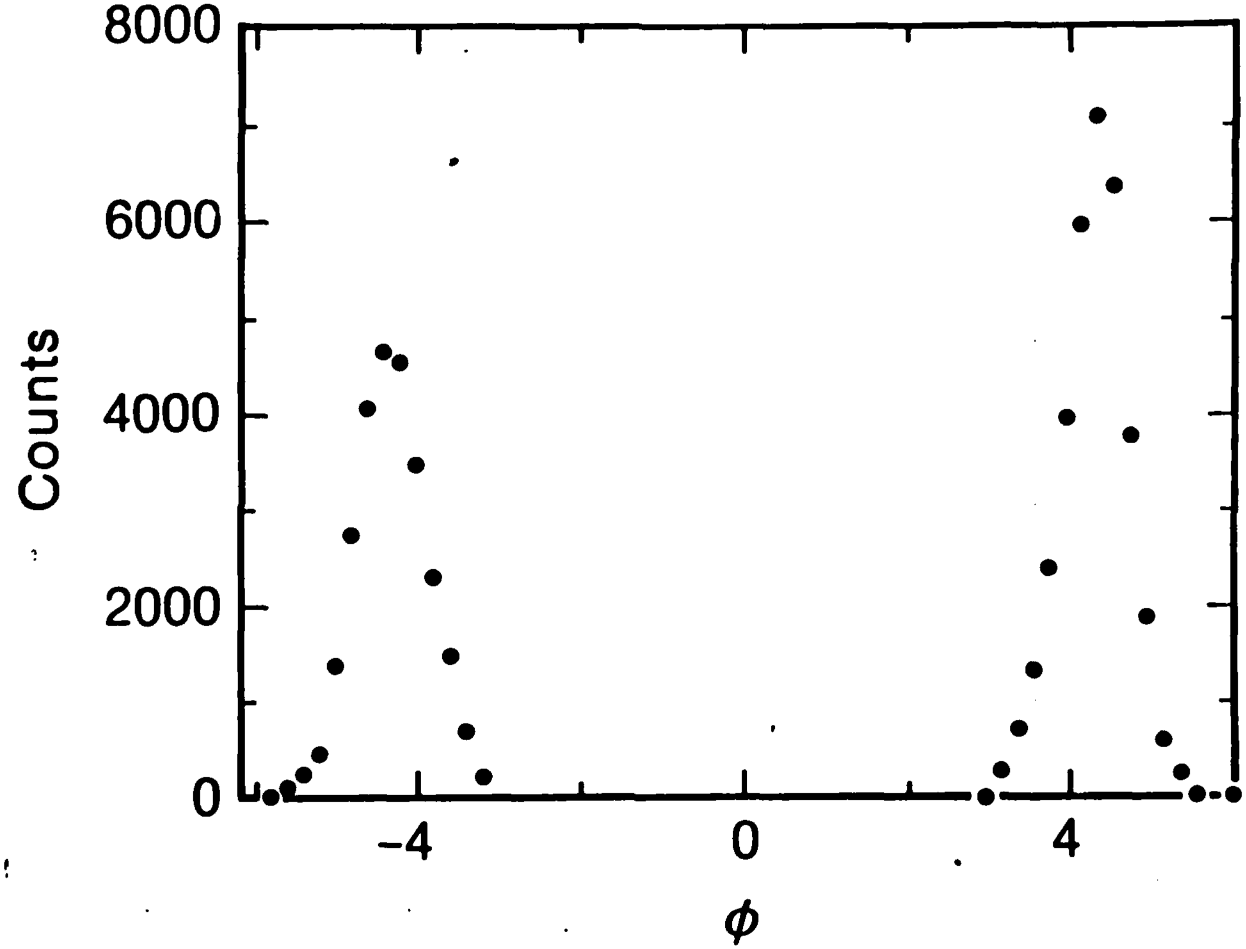
Figure 4. Schematic representation of one domain of UPD monolayer lead on silver (111). Open circles represent the silver atoms of the (111) surface and shaded circles represent the lead atoms. The Pb monolayer is incommensurate and one Pb atom is arbitrarily shown in the assumed 3-fold hollow site. The rotational epitaxy angle between Ag(110) and Pb(10) is 4.4°



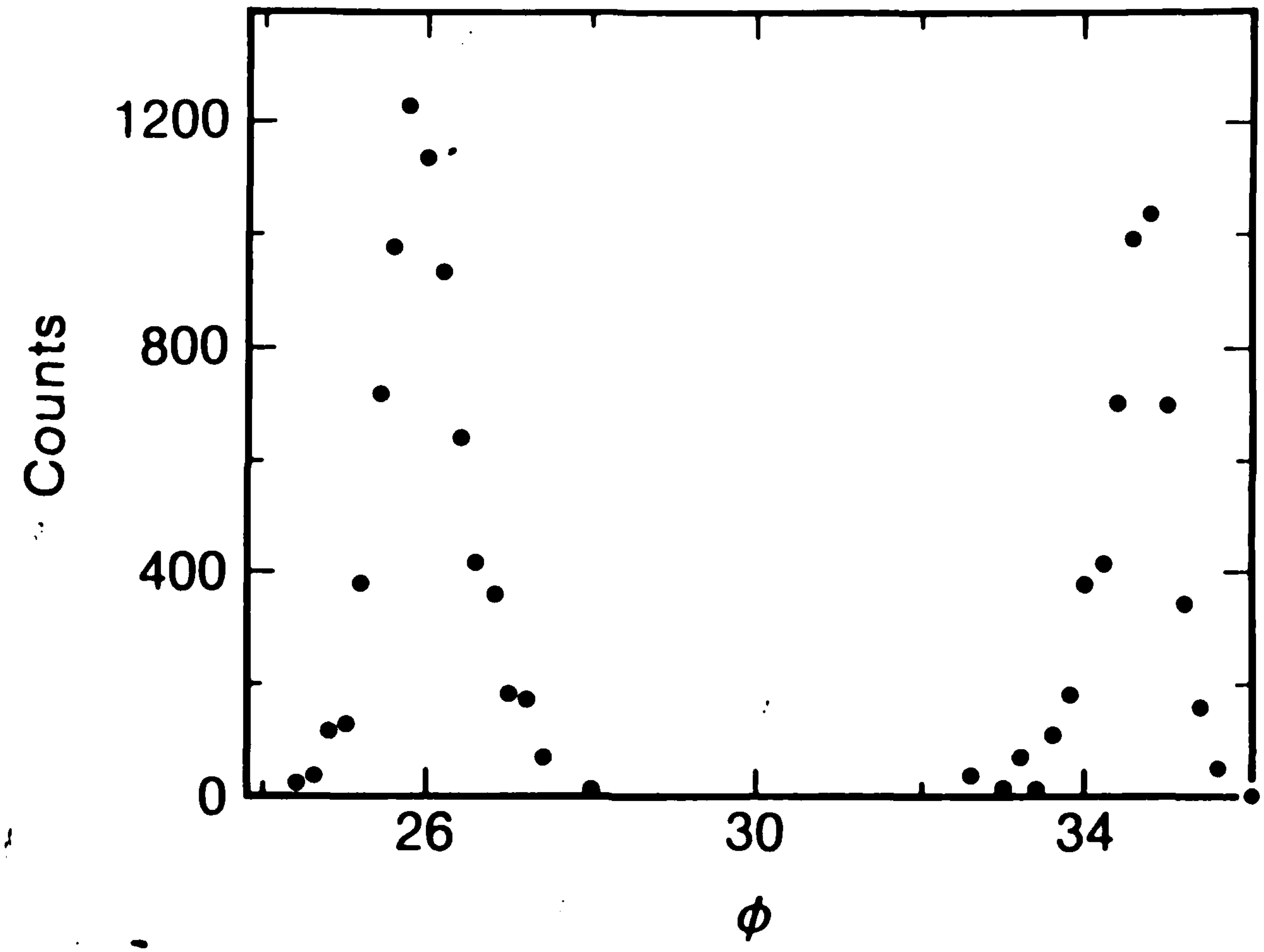

1

Electrochemical Cell: A) Silver (111) electrode, B) Ag/AgCl reference electrode, C) Platinum counter electrode, D) Polypropylene window, E) O-ring holding polypropylene to cell, F) External electrical connection to sliver electrode, G) Solution inlet, and H) Solution outlet.

Insert: Grazing incidence scattering geometry showing the incident angle $\alpha$, the output angle $\delta$, the scattering angle $\theta$, and theazimuthal angle $\phi$.

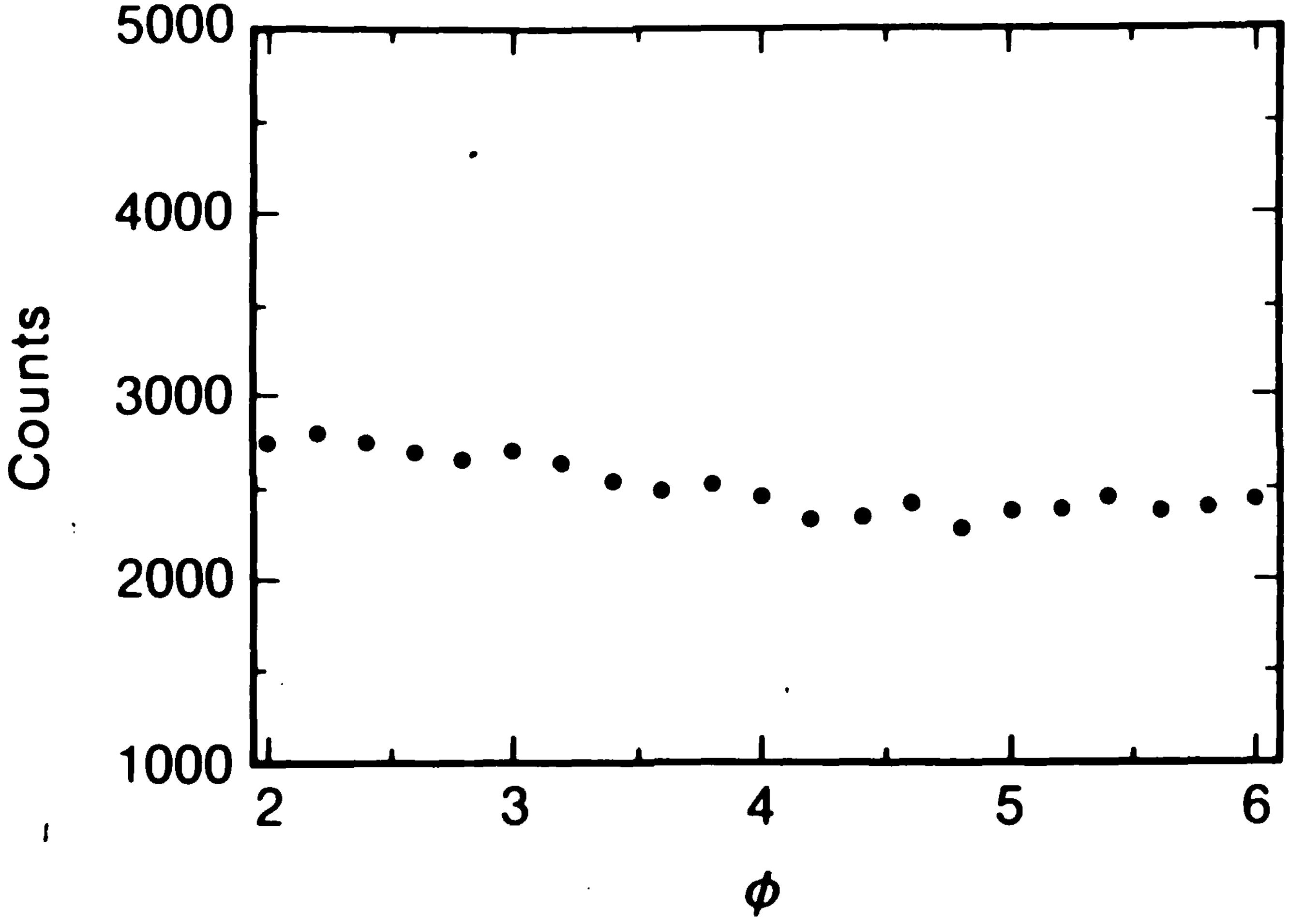



a) Rocking scans ($\theta$ $2\theta$ is fixed) of the lead (10) reflection at a scattering vector of 2.099 $Å^{-1}$, corresponding to the peak in the radial scans. The silver (110) direction is along $\phi$ = 330°

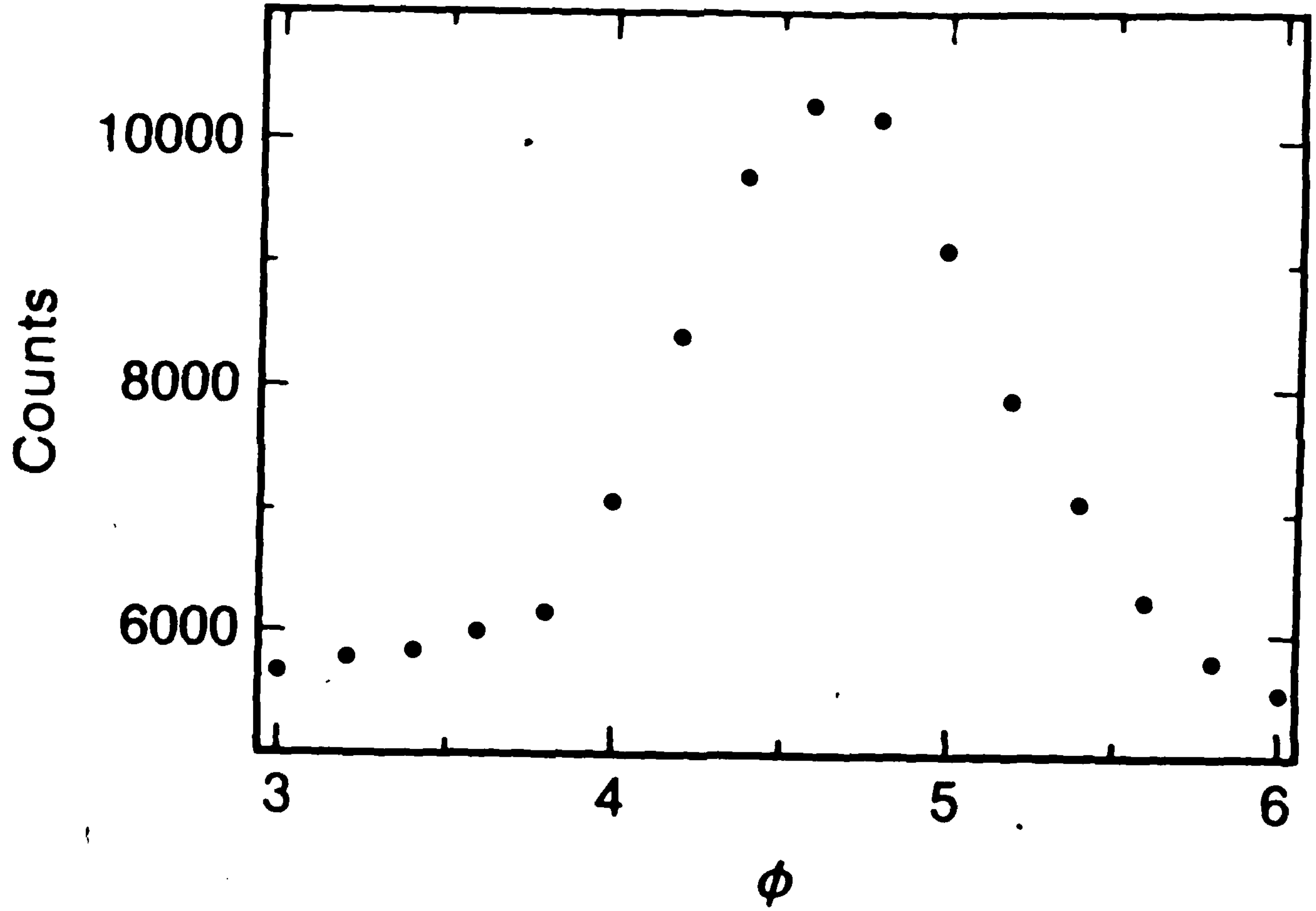



b) Rocking scans ($\theta$ $2\theta$ is fixed) of the lead (11) reflections at a scattering vector of 3.603 Å$^{-1}$, corresponding to the peak in the radial scans

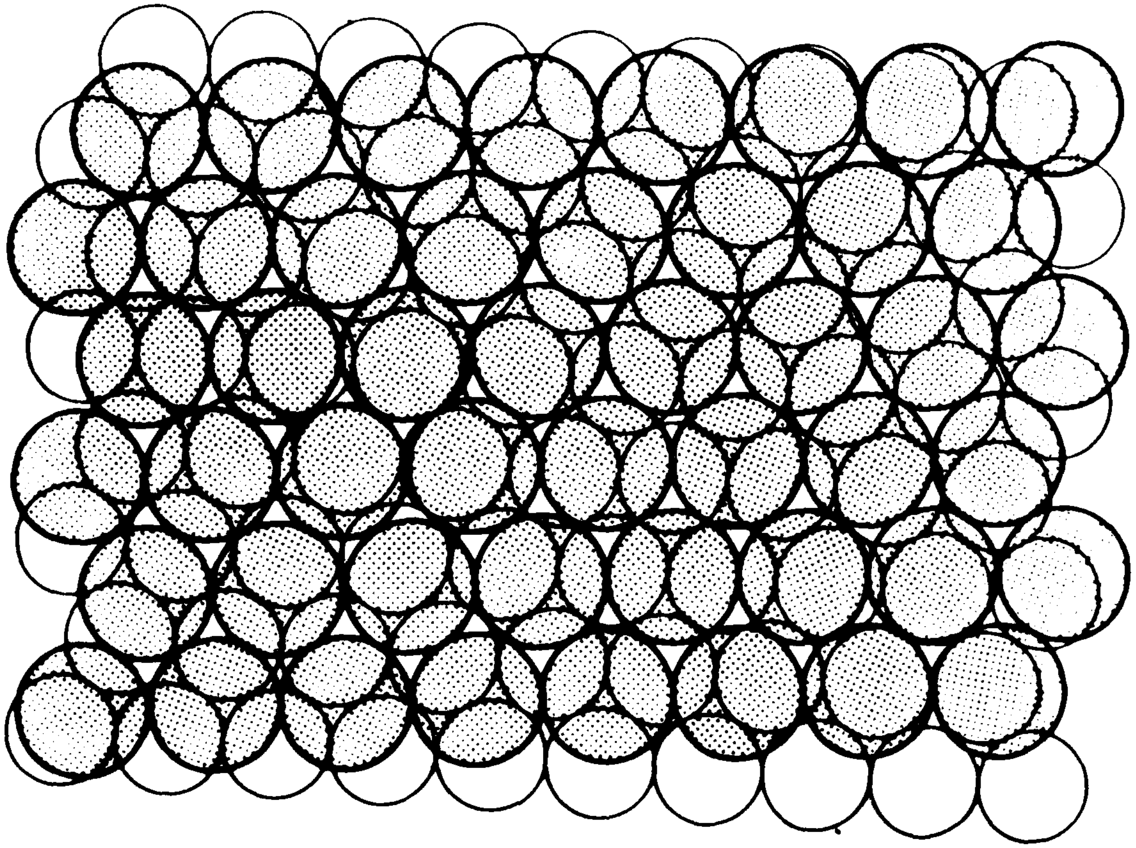
3 b




2b




2a



Schematic representation of one domain of UPD monolayer lead on silver (111). Open circles represent the silver atoms of the (111) surface and shaded circles represent the lead atoms. The Pb monolayer is incommensurate and one Pb atom is arbitrarily shown in the assumed 3-fold hollow site. The rotational epitaxy angle between Ag(110) and Pb(10) is 4.4°.

END

7-81

DTIC